

REPORT DOCUMENTATION PAGE				Form Approved OMB NO. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</p>					
1. REPORT DATE (DD-MM-YYYY)		2. REPORT TYPE New Reprint		3. DATES COVERED (From - To) -	
4. TITLE AND SUBTITLE BST FILMS GROWN BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION INCORPORATING REAL-TIME CONTROL OF STOICHIOMETRY				5a. CONTRACT NUMBER W911NF-07-1-0359	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER 611102	
6. AUTHORS DAVID A. BOYD, S. G. HIRSCH, C. HUBBARD, M. W. COLE				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAMES AND ADDRESSES California Institute of Technology Sponsored Research MC 201-15 1200 E. California Blvd. Pasadena, CA 91125 -0001				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSOR/MONITOR'S ACRONYM(S) ARO	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) 49731-EL.3	
12. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.					
13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
14. ABSTRACT We present preliminary results of metal organic chemical vapor deposition (MOCVD) growth of Ba _x Sr _{1-x} TiO ₃ (BST) thin films. Films were deposited on MgO, sapphire, Si, and Si/Pt/Ti substrates. Real-time monitoring of the precursor flux by UV absorption spectroscopy was used to control the composition of the films over the range 30 < x < 80. The films were characterized for a number of attributes including composition,					
15. SUBJECT TERMS BST, MOCVD, thin films, ferroelectrics					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON David Boyd
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU			19b. TELEPHONE NUMBER 626-395-4123

Report Title

BST FILMS GROWN BY METAL ORGANIC CHEMICAL VAPOR DEPOSITION INCORPORATING
REAL-TIME CONTROL OF STOICHIOMETRY

ABSTRACT

We present preliminary results of metal organic chemical vapor deposition (MOCVD) growth of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) thin films. Films were deposited on MgO, sapphire, Si, and Si/Pt/Ti substrates. Real-time monitoring of the precursor flux by UV absorption spectroscopy was used to control the composition of the films over the range $30 \leq x \leq 80$. The films were characterized for a number of attributes including composition, crystalline structure, and morphology.

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Continuation for Block 13

ARO Report Number 49731.3-EL
BST FILMS GROWN BY METAL ORGANIC CH ...

Block 13: Supplementary Note

© 2010 . Published in Integrated Ferroelectrics, Vol. Ed. 0 111, (1) (2010), (, (1). DoD Components reserve a royalty-free, nonexclusive and irrevocable right to reproduce, publish, or otherwise use the work for Federal purposes, and to authroize others to do so (DODGARS §32.36). The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

Approved for public release; distribution is unlimited.

BST Films Grown by Metal Organic Chemical Vapor Deposition Incorporating Real-Time Control of Stoichiometry

David A. Boyd,^{1,*} S. G. Hirsch,² C. Hubbard,² and M. W. Cole²

¹California Institute of Technology, Division of Engineering and Applied Science,
Pasadena, CA 91125, U.S.A.

²U.S. Army Research Laboratory, Weapons and Materials Research Directorate,
Aberdeen Proving Ground, Maryland 21005, U.S.A.

ABSTRACT

We present preliminary results of metal organic chemical vapor deposition (MOCVD) growth of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) thin films. Films were deposited on MgO, sapphire, Si, and Si/Pt/Ti substrates. Real-time monitoring of the precursor flux by UV absorption spectroscopy was used to control the composition of the films over the range $30 \leq x \leq 80$. The films were characterized for a number of attributes including composition, crystalline structure, and morphology.

Keywords: BST, ferroelectric thin films, MOCVD

INTRODUCTION

$\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) has desirable properties for microwave device applications. Features include a high dielectric constant, tunability, and that the Curie temperature can be adjusted with *modification of the Ba/Sr ratio* [1–3]. The motivation for our work is to develop a fabrication process that can reproducibly grow high quality BST thin films with good control of material properties over large area substrates. This is needed to obtain desired enhanced electrical properties and the performance consistency between devices. A manufacturing method that will support the affordability compliance and will mitigate the performance inconsistency is desirable.

Received August 16, 2009; in final form November 23, 2009.

*Corresponding author. E-mail: daboyd@caltech.edu

It is well known that the electronic properties of BST films are strongly influenced by the growth technique employed [1, 4]. The metal organic chemical vapor deposition [MOCVD] technique, which is an industry standard growth tool in both the semiconductor and microelectronics, provides precise control of film thickness with large area compositional uniformity, possesses high deposition rates, and enables wafer-to-wafer repeatability. In addition, MOCVD is a cost-efficient and scalable technique for a wide range of materials.

Simply stated, MOCVD involves exposing a heated substrate to flow of vaporized precursors that react with the substrate and deposit a film. The process variables include the precursor flux, substrate temperature, chamber pressure, and background pressure. The reactor in this experiment uses metalorganic chemical precursors. At room temperature, they are solids and must be heated to achieve a suitable vapor pressure; temperatures range from 130 to 235°C depending on the precursor. The precursors are contained in hermetic “bubblers” which are in turn housed in an oven. A gas such as Ar flows into the bubbler and carries vaporized precursor molecules to the reactor. For a single component film e.g. TiO_2 , the precursor flux can be determined from the vapor pressure of the precursor and the mass flow of the carrier gas, and it is not usually necessary to monitor and/or control the flux since changes in the vapor pressure of the precursor typically will only affect the instantaneous growth rate and not the overall composition. However, for multi-component films such as BST, control of the precursor flux is desirable for both achieving and maintaining the desired stoichiometry of the film throughout the growth run.

In the MOCVD reactor system used in these studies, we are able to control each component of the precursor flux in real-time. The control is based on real-time absorption measurements of the vaporized precursors before they reach the substrate. Each of the MOCVD precursors that we use absorbs light in the UV, and each of the bubblers has an in-line UV optical cell where the strength of the absorption is measured in real-time. Using the Beer-Lambert law and knowledge of the measured flow of carrier gas, temperature, and pressure, one can determine the molar flux of each precursor entering the reactor. The molar fluxes for Ba, Sr, and Ti are measured and computed in real-time, and these measured values are then used as control points in a PID control loop for each precursor source. The amount of precursor reaching the sample is determined by the flow of the carrier gas, which is controlled by an electronic mass flow controller (MFC) dedicated to each precursor source. These control loops allow control of the relative amounts of Ba, Sr, and Ti, and the overall total mass flow in $\mu\text{mole/min}$ reaching the substrates. In all, there are three independent control loops. This approach has worked very well for this reactor and has allowed us to grow multi-component oxide films including YBCO and ferroelectric PBT.

In this paper, we describe preliminary studies of MOCVD growth of BST films using the reactor and control system described above. We detail the progression of the growth conditions and characterization of the films grown. Finally, we will discuss improvements and next steps.

EXPERIMENT

The MOCVD reactor used in these experiments is a stagnation flow design that is configured with a vertical showerhead. The diameter of the copper showerhead is 50 mm, and the sample holder is placed 3.8 cm below in a sapphire holder that in-turn rests on the Inconel[®] “can”, which houses the graphite heater. The “can” temperature is read from three thermocouple attached to the inside of it, and the temperature is under closed loop control. The substrate temperature is based on previous calibrations involving an instrumented wafer. The reactor walls, gas tubing, and the showerhead are maintained at 250°C during growth by circulating oil to prevent condensation of the precursors. The total pressure in the reaction chamber is kept under closed loop control via a capacitance manometer on the chamber and a actuated valve on the vacuum pump. This arrangement has been shown to provide very uniform depositions. Details of the reactor design can be found elsewhere [5].

The key components of the reactor, which include the substrate temperature, the precursor mass flux, the system pressure, and all mass flows, are monitored and controlled by the reactor control code (RCC). The RCC has been recently re-written from the original DOS based software, and it now runs in the Lab View real-time Fieldpoint[®] controller. A real-time controller was included because this reactor is a complex, dynamic system that requires a several subsystems to all interact on-the-fly. In particular, the control of precursor delivery system, which is the basis for the composition control, involves three ultraviolet (UV) absorption spectrometers (one for each material component). The RCC has three main improvements: 1) The true real-time nature of the control. 2) The software runs on an embedded field point process which means that process runs independent of a local PC making it more immune to OS crashes. 3) The graphical user interface among other things allows us to view UV spectra in real-time and easily discern problems as well as track the numerous thermal sensors over the duration of the run.

The bubblers were prepared in following manner. Approximately 3.0 g of the strontium precursor, strontium(thd) (unadducted) were measured and then ground to a fine powder in a glove box under dry nitrogen. This was then mixed with 250 ml of 1/16” SS ball bearings. The coated bearings were placed into a stainless steel bubbler. Bubblers of barium (thd), unadducted and titanium diisopropoxide (thd2) were similarly prepared with 3.0 and 4.0 g, respectively. The precursors were obtained from SAFC.

RESULTS AND DISCUSSION

As with any new MOCVD process, the sample temperature, flow rates, and total mass flow would have to be determined empirically. It is important to note that although we can carefully control the precursor flux reaching the sample,

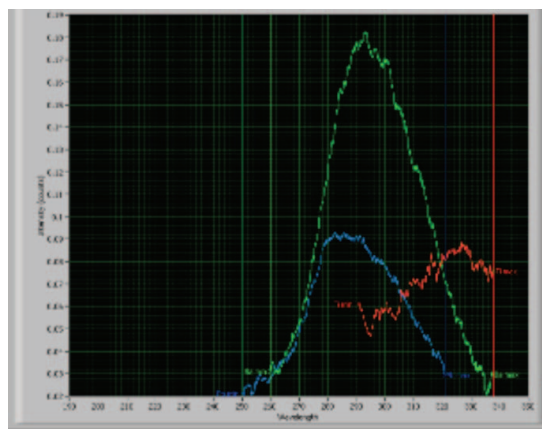


Figure 1. Optical absorption of the all three precursors, simultaneously measured in real time; the Sr(thd) signal is in blue, the Ba(thd) signal is green, and the Ti(thd2) is in red. (See Color Plate IV)

the final film composition will depend these parameters as well the reaction kinetics of the precursor and the substrate.

Our control of the precursor flux is a function of the vapor pressure of the precursor and the UV absorption features of the metalorganic precursors, and to date these values for Sr had not been measured nor were they available in the literature. The first practical issues were to determine the operating temperature of the Sr bubbler and the spectral window of the UV absorption. These were performed simultaneously; the UV absorption of the bubbler effluent was monitored as the bubbler temperature was increased and under a constant flow of Ar. An appreciable absorption was first observed at a bubbler temperature of 232°C. Shown in Fig. 1 is an image of the measured optical absorption of the all three precursors; the Sr(thd) signal is in blue, the Ba(thd) signal is green, and the Ti(thd2) is in red. We determined that the operating temperature for the Sr(thd) precursor was between 232 and 235°C, and that the absorption window for Sr was is 250–320 nm. These values as well as those for Ti and Bar are also summarized in Table 1.

Table 1
Bubbler temperatures and UV absorption spectral windows.

Precursor	$T_{\text{bubbler}}(^{\circ}\text{C})$	UV Spectral Window (nm)
Ba(thd)	237	260–235
Sr(thd)	232–235	250–320
Ti(thd2)	135–150	290–335

Table 2
Summary of the MOCVD reactor conditions (T in °C).

T_{growth}	Ba/ (Ba+Sr+Ti)	Sr/ (Ba+Sr+Ti)	Ti/ (Ba+Sr+Ti)	P_{bkg} (Torr)	Total Mass Flow (μ mole/min)	Flow O_2 (sccm)	Carrier Gas
600	0.3	0.2	0.5	15	1	2000	Ar

The initial growth conditions were based on our previous work with oxides [6]. The sample temperature was set to nominally 600°C, the total pressure was 15 Torr, and a 2000 sccm flow of oxygen was present during growth and cool-down. The temperature ramp rate was 15°C/minute. The growth conditions are summarized in Table 2. Sample substrates were MgO, Si, Si/Pt/Ti, and sapphire one of each was included per run. The carrier gas is mixed with nitrogen before the showerhead for a total flow of 5000 sccm. A 2000 sccm flow of O_2 flows during growth. The wafer is shielded from contaminants on the wall by a 5000 sccm “shroud” flow of N_2 .

The first three runs began with Ba:Sr:Ti; 30:20:50 stoichiometric (60:40) BST flow conditions. The growth time was an hour and the total mass flow rate was just below 0.1 μ mole/minute. We note that the molar absorptivities for the Sr and Ti precursors had not been measured nor were they found in the literature, that being said, all the values were set to 2.24×10^4 . The length of the UV cell is 10 cm. Shown in Fig. 2 are the real-time values of the computed ratios of Sr, Ba, and Ti. The ratios are determined from the measured absorptions in Fig. 1.

These films were analyzed by RBS and EDS, and we observed the following: 1) an excess of Ti and 2) the relative amount of Ti (Ba+Sr:Ti) was too high. A summary of Growth 3 results are in Table 3. The RMS roughness of the films from Growth 1 were measured by AFM, and found to vary per substrate: 16 nm for Pt-Ti-Si, 26 nm for Si, and 26 nm for sapphire. Shown in Fig. 3 is a cross sectional SEM image of one of the films of this series that

Table 3
Growth 3 molar ratios and composition values, as measured by EDS.

Ratio Setpoint	MgO	Si
Ba = 0.3	0.14	0.13
Sr = 0.2	0.12	0.14
Ti = 0.5	0.74	0.73
(Ba+Sr):Ti	0.35	0.37
Ba:Sr	54:46	49:51

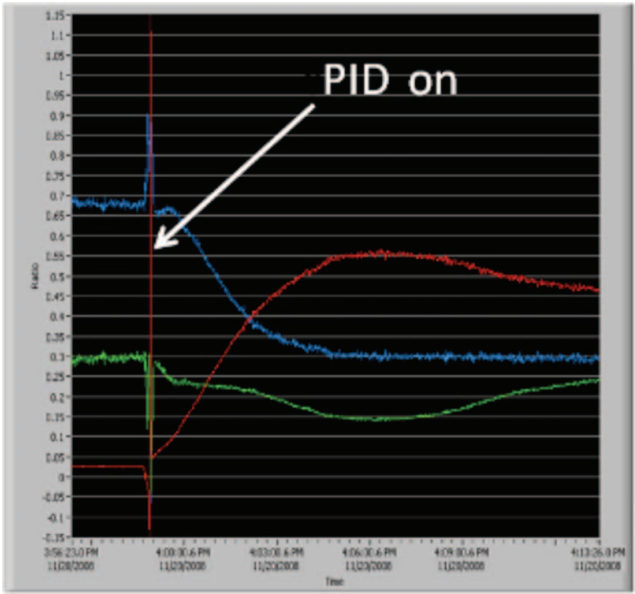


Figure 2. Images showing the precursor ratios with time; Ti is red, Sr is blue, and Ba is green. The ratio setpoints are: Ti = 0.47, Ba = 0.24, and Sr = 0.29. (See Color Plate V)

reveals a TiO_2 layer below the BST film. We traced this problem with the main reactor flow valve which switches the precursor flux from the “vent mode” where the precursor is vented to the “run mode” where precursor is delivered to the sample. Also in the first two runs, we observed Pb and Cu in the films that remained from previous studies. These disappeared in the subsequent growth runs.

Growth 5 achieved more desirable film stoichiometries. Following from the previous results, we reduced the amount of Ti precursor present in the flux.

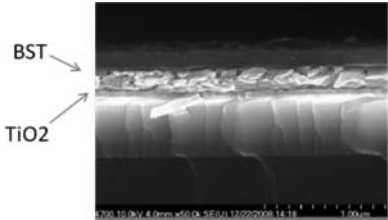


Figure 3. SEM cross-section showing the TiO_2 layer that formed below the BST film due to a faulty valve.

Table 4
Growth 5 molar ratios and composition values, as measured by EDS.

Ratio Setpoint	MgO	Sapphire	Si	Si/Pt/Ti
Ba = 0.47	0.184	0.157	0.165	0.194
Sr = 0.31	0.408	0.356	0.408	0.309
Ti = 0.22	0.408	0.489	0.427	0.498
(Ba+Sr):Ti	1.45	1.04	1.33	1.00
Ba:Sr	31:69	30:69	28:71	31:69

The PID parameters of the UV control were further adjusted to allow for a faster time response while avoiding overshoot or instabilities. Table 4 is a summary of the results for this run. The overall (Ba+Sr:Ti) ratios are closer to unity than Growth 3, but the (Ba:Sr) ratios were on nominally 30:70 instead of the desired 60:40. SEM cross-sectional images are shown in Figure 4. XRD spectra of the films, Figure 5, indicates polycrystalline growth.

For Growth 6, we increased the relative amount of Ba in the precursor flow. The measured (Ba:Sr) ratios were closer to what we desired nominally 75:25, however, the overall ratios (Ba+Sr:Ti) were still not at unity for all films. These results are summarized in Table 5. XRD spectra of these films, Figure 7, indicate polycrystalline growth for all the substrates. Figure 6 shows a cross-sectional SEM image of BST on Pt/Si/Ti.

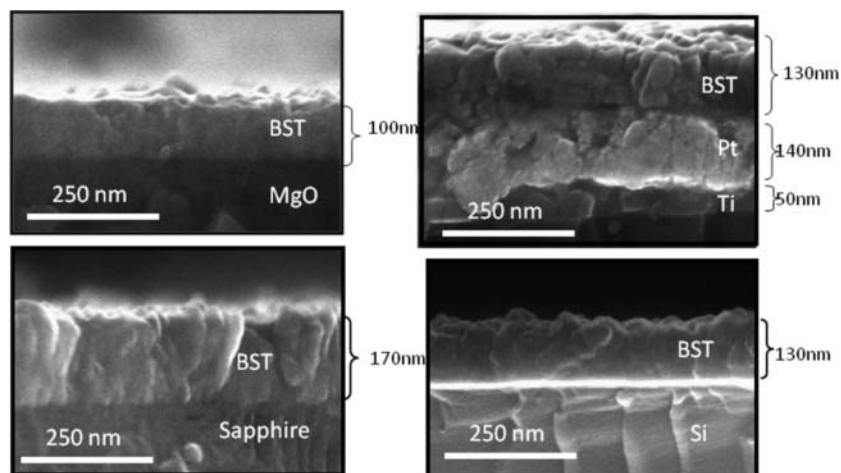


Figure 4. Growth 5 SEM cross-sectional images, showing the relative thicknesses of each layer.

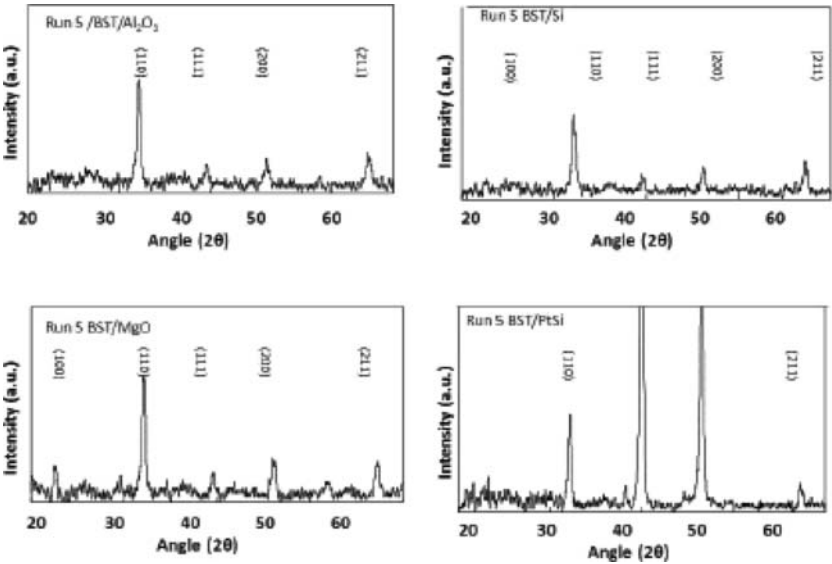


Figure 5. Growth 5 XRD spectra, indicating polycrystalline growth of BST on Al₂O₃, Si, MgO, and PtSi.

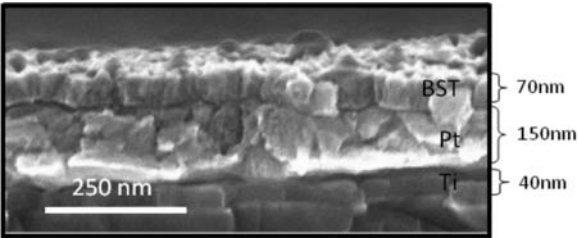


Figure 6. Growth 6 SEM cross-sectional image of the BST film on the Si/Pt/Ti substrate.

Table 5
Growth 6 molar ratios and composition values, as measured by EDS.

Ratio Setpoint	MgO	Sapphire	Si	Si/Pt/Ti
Ba = 0.61	0.443	0.363	0.565	0.448
Sr = 0.17	0.130	0.143	0.0	0.109
Ti = 0.22	0.427	0.493	0.435	0.443
(Ba+Sr):Ti	1.26	1.75	0.77	1.23
Ba:Sr	77:23	77:28	100:0	80:20

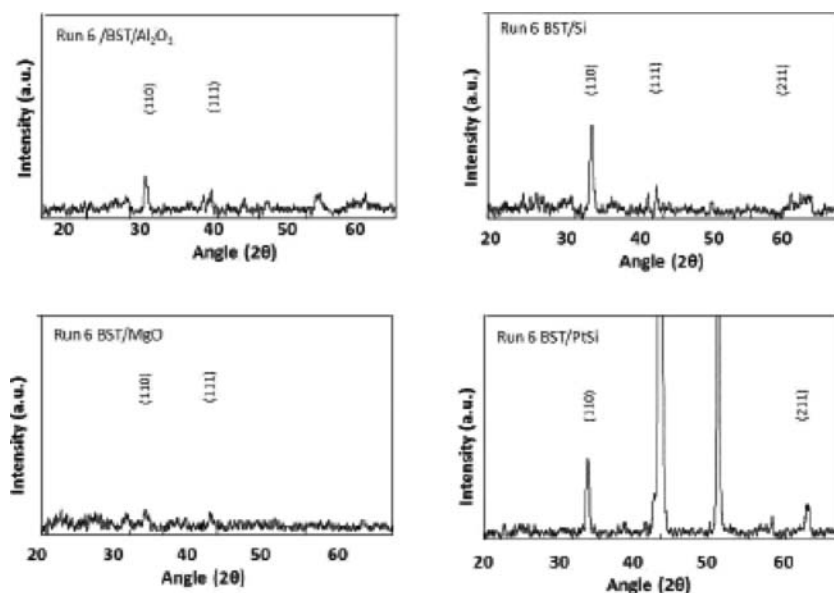


Figure 7. Growth 6 XRD spectra of the BST films on Al_2O_3 , Si, MgO, and PtSi.

Although we have not achieved 60:40 films in these first attempts, the Ba:Sr ratios achieved in to date do however, span the range of desirable compositions. These values are suitable for compositional graded heterostructures, for example, “up-graded films” (Ba:Sr) 30:70 to 90:10, from bottom to top. We note that all the substrates in each run were subjected to exactly the same precursor fluxes for a given run. However, as is evident from Figures 4 and 6, the film compositions can vary for each substrate. This is not surprising since the growth rates and even film morphology will depend in part on the substrate. Taking this into consideration, the growth parameters will need to be tailored for a particular substrate. In addition, we observed that the Ba precursor has the lowest reactivity, and it will be the limiting factor in the overall growth rate of these films. Measurements of the molar absorptivity are needed to for quantitative values of the precursor flux.

CONCLUSIONS

In summary, we have detailed our preliminary work on MOCVD growth of BST films on a variety of substrates. Films were grown over a wide range of Ba:Sr ratios using real-time control of the precursors flux. The range of stoichiometries achieved in the films covers a usable range desirable for compositionally graded films. More work will need to be done to optimize the films, and this

will involve exploring the parameter space of flow rates, substrate temperature, and cool-down conditions, but we believe that satisfactory films of constant composition are within reach.

ACKNOWLEDGMENTS

This work has been generously supported by the Army Research Office award # W911NF-07-1-0359.

REFERENCES

1. M. W. Cole, E. Ngo, S. Hirsch, J. D. Demaree, S. Zhong, and S. P. Alpay, *J. Appl. Phys.* **102**, 034104 (2007).
2. M. B. Okatan, M. W. Cole, S. P. Alpay, *J. Appl. Phys.* **104**, 104107 (2008).
3. M. W. Cole, R. G. Geyer, *Mech. Mater.* **36**, 1017 (2004).
4. M. W. Cole, W. D. Nothwang, P. C. Joshi, S. Hirsch, J. D. Demaree, *Integr. Ferroelectr.* **71**, 29 (2005).
5. A. B. Tripathi. Ph.D. thesis, California Institute of Technology, Pasadena CA, (2001).
6. M. El-Naggar, D. Boyd, and D. Goodwin, *J. Mater. Res.* **20**, 2969 (2005).